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Electron Affinity of Al_{13}: A Correlated Electronic Structure Study

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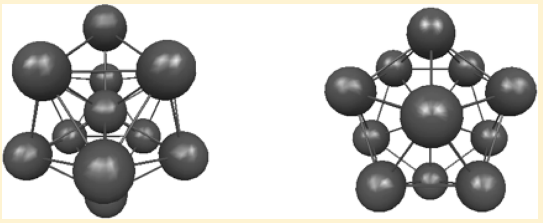
ABSTRACT: Neutral and anionic 13-atom aluminum clusters are studied with high-level, fully ab initio methods: second-order perturbation theory (MP2) and coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T)). Energies and vibrational frequencies are reported for icosahedral and decahedral isomers, and are compared with density functional theory results. At the MP2 level of theory, with all of the basis sets employed, the icosahedral structure is energetically favored over the decahedral structure for both the neutral and anionic Al_{13} clusters. Hessian calculations imply that only the icosahedral structures are potential energy minima. The CCSD(T)/aug-cc-pVTZ adiabatic electron affinity of Al_{13} is found to be 3.57 eV, in excellent agreement with experiment.



INTRODUCTION

Al_{13}^- is a remarkably stable closed-shell cluster that has been referred to as a "superhalogen".[1] Therefore, Al_{13}^- is of potential interest as an anion in ionic liquids. Experimental studies suggest that Al_{13}^- is highly symmetric[2] and cannot be etched by oxygen.[3] These properties are in agreement with its description as a "magic cluster" according to the jellium model,[4] in which the nuclear geometry of the cluster is approximated as a spherical charge distribution interacting with delocalized valence electrons. This model predicts that 2, 8, 20, 40, and so forth valence electrons will correspond to stable, closed-shell clusters. Al_{13}^- has 40 valence electrons.

The structure of Al_{13}^- is widely accepted to be icosahedral,[1,5] having two five-atom "rings" that are staggered with respect to one another. For the neutral Al_{13} cluster, previous density functional theory (DFT) studies[6−8] have predicted two possible isomers: a distorted icosahedron and a distorted decahedron (Figures 1 and 2). In the decahedral structure, the two five-atom "rings" are aligned. A study[6] using the BPW91 functional[9] and the LANL2DZ basis set with the Hay−Wadt relativistic effective core potential[10] predicts the neutral Al_{13} decahedron to be energetically preferred over the icosahedron by 0.43 eV. A study[7] using the hybrid B3LYP functional[11] with the same LANL2DZ likewise finds the neutral decahedron to be 0.41 eV lower in energy than the icosahedron. However, the energy ordering reverses when an all-electron calculation is performed:[8] the icosahedron is 0.23 eV lower in energy at the BPW91/6-311G(d) level of theory. The authors describe the isomers as nearly degenerate within the accuracy of the calculations.[6,8]

Using the local spin density approximation with the VWN functional,[12] Mananes et al.[13] conclude that the neutral Al_{13} cluster takes on a distorted icosahedral D_{3d} geometry. Han, Jung, and Kim[14] show that B3LYP with the aug-cc-pVDZ basis set[15] overdistorts the neutral Al_{13} cluster, producing a heavily distorted C_s structure as the ground state. This B3LYP/aug-cc-pVDZ structure does not resemble either an icosahedron or a decahedron. At this level of theory, the D_{3d} geometry is 0.111 eV higher in energy than the C_s structure.[14] The hybrid PBE functional[16] with the aug-cc-pVDZ basis set, however, predicts a D_{3d} ground state, with the C_s structure 0.258 eV higher in energy.[17]

Other studies describe the decahedral and icosahedral neutral isomers as competing structures due to their small energy difference.[18] A Car−Parrinello study[19] finds a single, well-defined, slightly distorted icosahedral minimum energy structure for Al_{13}, while a model potential basin-hopping Monte Carlo simulation[20] finds the point group of Al_{13} to be I_h. A study[21] utilizing a genetic algorithm coupled with a tight-binding potential, whose low-energy structure candidates were further optimized with local density approximation DFT, finds an icosahedral ground state for Al_{13}. In this work, the decahedral structure is 0.48 eV higher in energy, and the heavily distorted C_s structure discussed previously (found as the ground state with B3LYP/aug-cc-pVDZ in ref 14) lies about 0.02 eV higher still.[20]

Al_{13}^- has been the subject of a coupled cluster study,[21] in which the singles + doubles + noniterative pertubative triples, CCSD(T),[22] method was employed. CCSD(T) single point energy calculations, using the 6-311G(d)[23] basis, were performed on the icosahedral and decahedral isomers of Al_{13}^- after optimization with the Hartree−Fock (HF)/3-21G(d) method. At the CCSD(T)/6-311G(d) level of theory, the icosahedron is 0.54 eV lower in energy than the decahedron. Furthermore, the authors report that electron propagator[24] vertical electron detachment energy (VEDE) predictions for the icosahedron are in much closer agreement with experimental photoelectron spectra than are the predicted VEDEs for the decahedron.[21]

Distortion from the perfect icosahedral and perfect decahedral structures in the neutral isomers has been attributed to the Jahn−Teller effect.[6,8] However, a thorough molecular orbital investigation of this phenomenon has not been presented, to the authors' knowledge.

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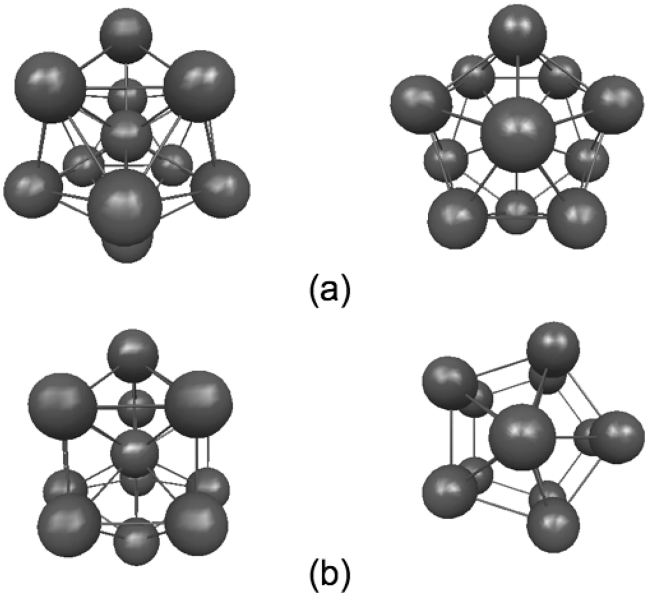

Figure 1. Side and top views of (a) the icosahedral and (b) the decahedral geometries of the 13-atom aluminum cluster. The anion takes on perfect (nondistorted) geometries while the neutral cluster geometries are Jahn−Teller distorted.

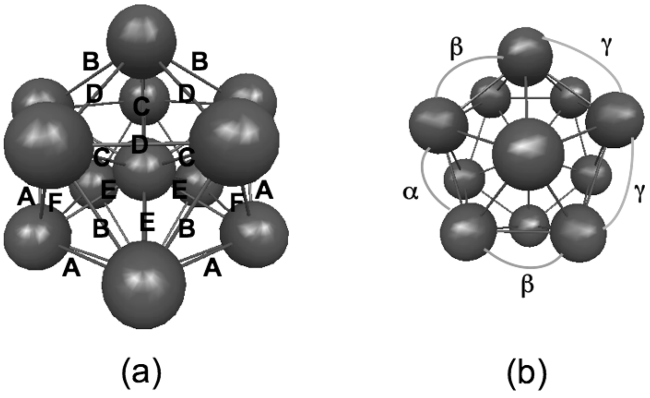

Figure 2. Bond (a) lengths and (b) angles of the Jahn−Teller distorted icosahedral structure of neutral Al_{13}. In (a), A = 2.901 Å, B = 2.772 Å, C = 2.659 Å, D = 2.971 Å, E = 2.734 Å, and F = 2.764 Å. In (b), representative angles α = 60.0°, β = 57.6°, and γ = 63.2°. For the perfect icosahedral anion, all bond lengths to interior atom are 2.685 Å and between exterior atoms are 2.823 Å; all angles are 60.0°. Bond lengths and angles determined with MP2/6-311+G(2d).

Explicit mention of vibrational frequencies or the outcome of Hessian (matrix of energy second derivatives) calculations for Al_{13} species is also rare in the literature, with the notable exception of ref 14 for $Al_{13}H$. Hessian matrices in particular are important, since a positive definite Hessian (all-real vibrational frequencies) indicates that one has found a local minimum on the potential energy surface. However, one or more negative Hessian eigenvalues (imaginary frequencies) indicate that the found structure is a saddle point. A single imaginary frequency suggests a transition state. Most of the works cited in the previous paragraphs do not provide such information.

Examining the adiabatic electron affinity of Al_{13} gives insight into the importance of geometric relaxation upon electron attachment, as well as an assessment of the accuracy of the geometry optimizations. The vertical electron affinity (VEA) is the energy difference between the neutral cluster and the anionic cluster at the geometry of the neutral cluster. However, the adiabatic electron affinity (AEA) is the energy difference between the neutral and anionic clusters at their respective optimized geometries. So, the AEA includes relaxation effects that occur after the electron attachment occurs. Similar values for the vertical and adiabatic electron affinities imply that the neutral and anionic clusters have similar geometries. Since experimental results for electron affinities may be available even when experimental structures are not, an energy difference between theoretically determined structures that is in good agreement with experimental electron affinity values can imply the validity of the theoretical structures. A photoelectron spectroscopy study[2] found the adiabatic electron affinity of the neutral cluster to be 3.62 ± 0.06 eV. This provides impetus for the present computational analysis. In addition, while the structure of the anionic cluster Al_{13}^- appears to be well established, there is clearly little consensus on the structure of the neutral cluster, or on the relative energies of the two species. Therefore, an accurate determination of the structure of Al_{13} and the related energetics is important.

METHODS

Second-order Moller−Plesset perturbation theory (MP2)[25] was employed as a means of studying the neutral and anionic Al_{13} clusters with a fully ab initio method that includes electron correlation. MP2 geometry optimizations and seminumerical Hessians (finite differencing of analytic gradients) were obtained using three basis sets: LANL2DZ, which uses an effective core potential (ECP), and the all-electron Pople bases 6-31+G(d)[26] and 6-311+G(2d).[23] Additionally, single-point energy calculations on the MP2/6-311+G(2d) optimized icosahedral structures of anionic and neutral Al_{13} were carried out using coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T)[22]) with the aug-cc-pVTZ basis set. Theoretical values for the adiabatic ionization potential of Al_{13}^- were determined by taking the energy difference between the anionic and neutral clusters at their respective optimized geometries.

For comparison, optimizations and seminumerical Hessian calculations were also performed using the same three basis sets with the B3LYP and BPW91density functionals, using the geometries of Rao and Jena[6] as a starting point.

The CCSD(T) single-point energies were determined using Molpro.[27] All other calculations were performed with the GAMESS (General Atomic and Molecular Electronic Structure Theory) quantum chemistry software package.[28]

RESULTS AND DISCUSSION

At the MP2 level of theory, with any of the basis sets examined, the icosahedral structure is energetically favored over the decahedral structure for both the neutral and anionic Al_{13} clusters (Tables 1 and 2). Additionally, Hessian calculations imply that only the icosahedral structures are potential minima, having no imaginary frequencies (Tables 3 and 4).

First, consider the relative energies listed in Tables 1 and 2. MP2 predicts that the icosahedral Al_{13}^- structure is lower in energy than the decahedral structure with all basis sets, although the LANL2DZ effective core potential (ECP) predicts an energy difference that is too small. Indeed, this basis set is inadequate at

Table 1. Energy Difference (in eV) between the Decahedral (D_{5h}) and Icosahedral (D_{5d}) Isomers of Anionic Al_{13}[a]

	BPW91	B3LYP	MP2
LANL2DZ	−0.12	−0.36	0.50
6-31+G(d)	0.44	0.17	1.59
6-311+G(2d)	0.43	0.17	1.40

[a] A positive value indicates that the icosahedral structure is lower in energy than the decahedral structure; a negative value indicates the decahedron is preferred.

Table 2. Energy Difference (in eV) between the Distorted Decahedral (C_s) and Distorted Icosahedral (D_{3d}) Isomers of Neutral Al_{13}[a]

	BPW91	B3LYP	MP2
LANL2DZ	−0.31	−0.53	0.04
6-31+G(d)	0.26	−0.01	1.02
6-311+G(2d)	0.26	0.03	0.92

[a] A positive value indicates the distorted icosahedral structure is lower in energy than the distorted decahedral structure; a negative value indicates the distorted decahedron is preferred.

Table 3. Number of Imaginary Frequencies Found for Each Isomer of the Anionic Al_{13} Cluster

	icosahedron (D_{5d})			decahedron (D_{5h})		
	BPW91	B3LYP	MP2	BPW91	B3LYP	MP2
LANL2DZ	5	5	0	0	2	1
6-31+G(d)	0	0	0	1	0	N/A
6-311+G(2d)	0	0	0	1	1	1

Table 4. Number of Imaginary Frequencies Found for Each Isomer of the Neutral Al_{13} Cluster

	distorted icosahedron (D_{3d})			distorted decahedron (C_s)		
	BPW91	B3LYP	MP2	BPW91	B3LYP	MP2
LanL2DZ	4	6	0	0	0	0
6-31+G(d)	0	2	0	2	1	1
6-311+G(2d)	0	0	0	2	2	7

all levels of theory. Both functionals, BPW91 and B3LYP, predict the incorrect energy order when the ECP basis set is used. Even with the larger, all-electron basis sets, DFT predicts an energy difference that is too small, even though the correct energy order is predicted. Similar comments apply to the neutral Al_{13} cluster. The ECP basis set predicts energy differences that are too small or the wrong sign, and the DFT methods with the all-electron basis sets predict the correct energy order with a magnitude that is too small.

MP2 consistently predicts that the icosahedral structure is a minimum on both the Al_{13} and Al_{13}^- potential energy surfaces. For the anion, MP2 predicts the decahedral structure to be a first order saddle point (transition state). The two functionals are less definitive, since their prediction regarding the nature of this stationary point depends on the basis set that is used. For the largest basis set, all three methods agree that the decahedral

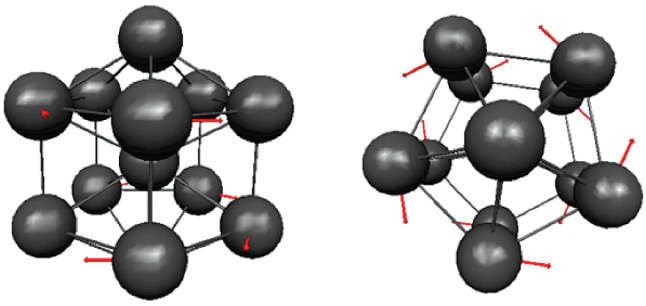

Figure 3. Side and top views of the imaginary frequency mode from the anionic cluster constrained to D_{5h} symmetry. This torsional mode suggests the structure will naturally take icosahedral symmetry.

species is a transition state. For the neutral Al_{13} radical, the decahedral species is clearly not a minimum on the potential energy surface. The number of imaginary frequencies depends on both the method and the basis set, and the ECP is clearly unreliable.

The icosahedral anion has perfect I_h symmetry (specified as D_{5d} in practice). At the MP2/6-311+G(2d) level of theory, the nearest neighbor bond distances are 2.823 Å between the outer twelve atoms and 2.685 Å from the outer atoms to the interior atom. This agrees nearly exactly with B3LYP/6-311+G(2d) (2.820 Å exterior, 2.682 Å interior) and very closely with BPW91/6-311+G(2d) (2.811 Å exterior, 2.673 Å interior). The decahedral anion with D_{5h} symmetry has one imaginary frequency [112i cm^{-1} with MP2/6-311+G(2d)], consisting of a torsional motion that would rotate the aligned pentagonal "rings" to a staggered configuration as in the icosahedron (Figure 3). As noted above, this suggests the decahedral structure is a transition state.

The neutral (doublet radical) structure is distorted from its closed shell anionic analogue. When constrained to the same D_{5d} symmetry as the undistorted icosahedral anion, the neutral structure exhibits multiple imaginary frequencies. Consistent with a previously proposed distorted icosahedral D_{3d} structure,[13] the neutral cluster has a positive definite Hessian when relaxed to D_{3d} symmetry. At the MP2 level of theory, this distortion from D_{5d} to D_{3d} lowers the energy by 0.2 eV. Decahedral structures for the neutral cluster exhibit multiple imaginary frequencies, whether constrained to (undistorted) D_{5h} symmetry or relaxed to (distorted) C_s symmetry.

The MP2/6-311+G(2d) neutral icosahedral bond lengths range from 2.901 Å to 2.734 Å. The B3LYP/6-311+G(2d) and BPW91/6-311+G(2d) ranges of distances are 2.992 Å to 2.723 Å and 2.964 Å to 2.663 Å, respectively. Bond lengths as shown in Figure 2 can be found in Table 5.

The distortion in the neutral clusters arises from the Jahn−Teller effect.[6,8] This requires the unequal occupancy of two (or more) degenerate orbitals. Jahn−Teller distortion removes the degeneracy by lowering the symmetry. Orbital diagrams of the anionic (D_{5d} icosahedral) and neutral (D_{3d} distorted icosahedral) Al_{13} clusters appear in Figure 4. The highest occupied molecular orbitals (HOMO) of the anion (Figure 4(a)) are doubly degenerate orbitals with E_{1u} symmetry. They are isoenergetic with a second doubly degenerate set of orbitals having E_{2u} symmetry. Removing an electron from the E_{1u} HOMO to produce neutral Al_{13} yields the unequally occupied degenerate orbitals that lead to Jahn−Teller distortion. The distortion of the neutral cluster produces a singly occupied, nondegenerate HOMO with A_{2u}

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Table 5. Bond Lengths (Å) in Distorted Icosahedral (D_{3d}) Geometry of Neutral Al_{13}[a]

	BPW91	B3LYP	MP2
A	2.879	2.898	2.901
B	2.762	2.763	2.772
C	2.663	2.677	2.659
D	2.964	2.992	2.971
E	2.712	2.723	2.734
F	2.763	2.780	2.764

[a] Letters A−F correspond to bonds shown in Figure 2(a). Calculations performed with 6-311+G(2d) basis set.

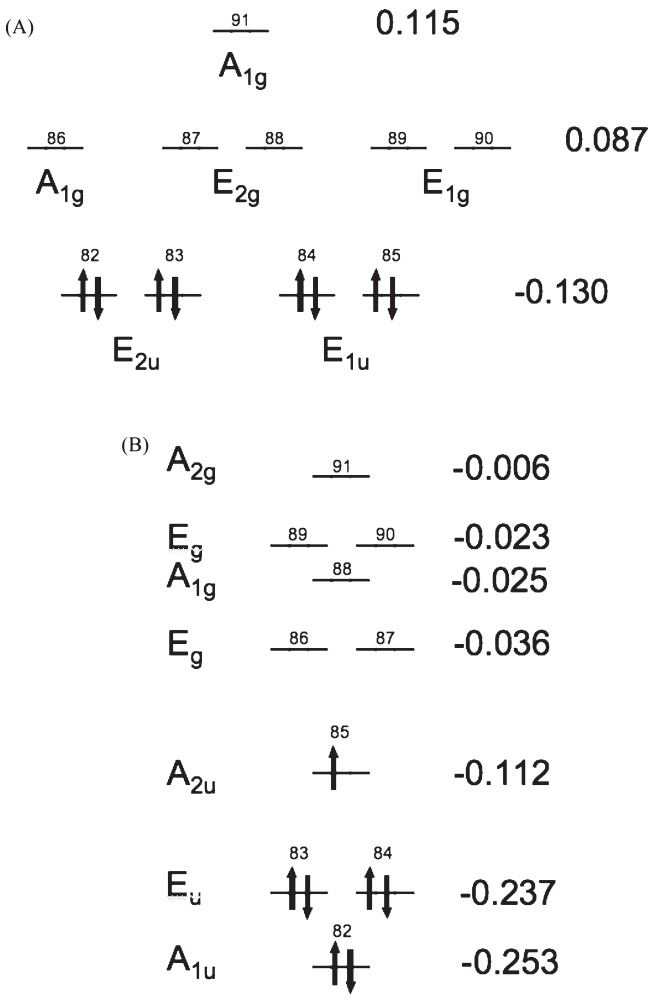

Figure 4. Orbital diagram of (A) anionic and (B) neutral Al_{13} clusters. Orbital symmetries and energies (in hartree) shown for a selection of orbitals near the HOMO−LUMO. The anion has perfect icosahedral symmetry (D_{5d} in practice), while the neutral has distorted icosahedral symmetry (D_{3d}).

symmetry (Figure 4(b)). The Al_{13} HOMO is nondegenerate A_{2u} even when the neutral cluster is constrained to the same (nondistorted) icosahedral geometry as the anion.

The adiabatic electron affinity of Al_{13} is the energy difference between the optimized neutral and anionic structures (Table 6). Relative to the experimental value of 3.62 ± 0.06 eV, MP2 overestimates the adiabatic electron affinity by about 0.2 eV when either Pople basis set is used, but underestimates it by 0.15 eV with the LANL2DZ basis. DFT calculations underestimate this value to an extent that is dependent on the functional. With BPW91, the calculated adiabatic electron affinity is about 0.3 eV lower than the experimental value. B3LYP yields a more significant deviation, approximately 0.5 eV lower. Single point energy calculations using CCSD(T)/aug-cc-pVTZ on the geometries obtained with MP2/6-311+G(2d) optimizations yields an adiabatic electron affinity of 3.57 eV, in excellent agreement with the experimental value.

Table 6. Adiabatic Electron Affinity of Al_{13}[a]

	BPW91	B3LYP	MP2	CCSD(T)
LanL2DZ	3.28	3.06	3.47	
6-31+G(d)	3.34	3.16	3.83	
6-311+G(2d)	3.33	3.14	3.86	3.57

[a] Units of eV. These values are the energy difference between the neutral icosahedral (D_{3d}) and anion icosahedral (D_{5d}) structures. Experimental value is 3.62 ± 0.06 eV (Ref 2).

The MP2/6-311+G(2d) vertical ionization potential (the energy difference between the optimized neutral cluster and the cation at the neutral cluster geometry) is 6.93 eV for the decahedron and 7.21 eV for the icosahedron. DFT[8] with the BPW91/6-311G(d) functional predicts a vertical ionization potential for the decahedron to be 6.48 eV and that of the icosahedron to be 6.79 eV. An experimental study[29] reports the vertical electron affinity to be 6.45 ± 0.05 eV. So, there is a very large geometry relaxation effect on the observed electron affinity.

CONCLUSIONS

A small, frozen core basis set like LANL2DZ is inadequate to describe the electronic structure of Al_{13} clusters, especially when used with density functional theory calculations. Compared to results found with the larger, all-electron Pople basis 6-311+G(2d), DFT calculations with LANL2DZ show a reversal of the energetic ordering of the icosahedral and decahedral isomers of both neutral and anionic Al_{13}.

DFT predictions vary with the choice of functional, notably in the case of the ground state neutral Al_{13} structure. B3LYP with either all-electron basis assigns very nearly equal energies to the decahedral and icosahedral geometries (differing by hundredths of an eV), while BPW91 favors the icosahedron by 0.26 eV. MP2 predicts that the neutral icosahedron is approximately 1 eV more stable than the decahedron. B3LYP also underestimates the energy difference between isomers of the anionic cluster, giving 0.17 versus 0.43 eV for BPW91/6-311+G(2d) and 1.40 for MP2/6-311+G(2d). However, icosahedral bond lengths and angles determined with B3LYP, rather than BPW91, more closely match those determined with MP2. Hessian calculations, which can show whether the proposed structure is indeed a local minimum on the potential energy surface, are also dependent on the choice of functional.

The Al_{13} adiabatic electron affinity value of 3.57 eV found via CCSD(T)/aug-cc-pVTZ single point energy calculations on MP2/6-311+G(2d) geometries is in excellent agreement with the experimentally determined value[2] of 3.62 ± 0.06 eV.

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